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**Adhesive composition**

5 The invention relates to an adhesive composition, to  
the use of such an adhesive composition, to a method of  
joining substrates using such an adhesive composition,  
and to a device having at least one region which has  
been prepared with such an adhesive composition for  
joining to a substrate. The invention relates in  
10 particular to pressure-sensitive hot-melt adhesives and  
to their use, particularly for bonding substrates to  
skin.

15 Known from the document US 5,028,485 is a pressure-  
sensitive adhesive composition suitable for skin  
contact. It comprises a polymer, a copolymer or a  
mixture of polymer and/or copolymer; additionally,  
customary additives may be provided. Essential to the  
invention is the addition of relatively high  
20 concentrations of 1-20% by weight of one or more silane  
compounds, which improves the wet peel strength.  
However, the use of a reactive silane compound is  
associated with considerable drawbacks:

- 25 - possible classification of the silane compound as  
a hazardous substance may result in a hazard  
labeling obligation;
- the adhesive gives off a pronounced odor which is  
30 perceived as unpleasant;
- there is an allergenic potential for skin  
irritation.

35 The use of sulfonated polyesters in hot-melt adhesives  
is known - from the document US 6,428,900, for example.  
According to that document, however, adhesive  
compositions containing 10% to 90% of a branched,

sulfonated copolyester, and bonds produced using them, dissolve in the presence of water.

Furthermore, from the document EP 761 795 B1, it is known to mix further elastomeric polymers, such as styrene-containing block copolymers, for example, additionally, if desired, into sulfonated copolyesters. These adhesive compositions are preferably not pressure-sensitive; moreover, for many applications, including in particular those in the medical sector, as for example for self-adhesive drapes for bonding to skin, the wet peel strength is inadequate, owing to the inherent water-solubility of the sulfonated copolyesters, especially branched sulfonated copolyesters.

US 6,025,071 describes a detachable ("removable grade") hot-melt adhesive comprising a styrene-isoprene-styrene block copolymer having a diblock fraction of more than 50%. It is assumed that the high diblock fraction contributes to improved adhesion to the base substrate. For adhesive compositions of this kind it has emerged, however, that for many applications, particularly for bonding to the skin, the wet peel strength is inadequate.

It is therefore an object of the invention to avoid the drawbacks of the known art and so in particular to provide an adhesive composition which has improved wet peel strength, particularly to skin, and which is also unproblematic in its handling and compatibility. It is a further object of the invention to provide an adhesive composition which can be applied inexpensively and without special precautions.

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In accordance with the invention these objects are achieved by means of an adhesive composition and the use of such a composition, and a method using such an

adhesive composition, and also a device, having the features of the independent claims.

5 An adhesive composition according to the invention comprises an elastomeric block copolymer having a diblock fraction of more than 40%, preferably of more than 55%, more preferably of more than 70%, and a sulfonated copolyester, in particular a branched copolyester. The adhesive composition may further  
10 comprise, if desired, further additives such as tackifiers and/or plasticizers and/or stabilizers.

By an elastomeric block copolymer is meant, here and below, in particular, polymers of the general formula  
15 A-B or A-B-A, A denoting a thermoplastic block and B a block having rubber-elastic and/or elastomeric properties, especially rubberlike properties. The thermoplastic A block is preferably a polymer of one or more alkenylaromatics, especially styrene (with which  
20 particularly advantageous properties have been achievable) and its homologs, e.g.,  $\alpha$ -methylstyrene; 4-substituted styrenes, e.g., 4-(4-phenyl-n-butyl)styrene, and in particular 4-alkylstyrenes, e.g., 4-methylstyrene, 4-n-propylstyrene, and 4-cyclohexylstyrene; 5-substituted styrenes, especially  
25 5-alkylstyrenes, e.g., 5-tert-butylstyrene; 3,5-disubstituted styrenes, especially 3,5-dialkylstyrenes, e.g., 3,5-diethylstyrene and 3,5-di-n-butylstyrene; 2,4-disubstituted styrenes, e.g., 2-ethyl-4-benzylstyrene, and in particular 2,4-dialkylstyrenes,  
30 e.g., 2,4-dimethylstyrene; and vinyltoluene. The rubber-elastic and/or elastomeric, especially rubberlike, B block is preferably a polymer of a conjugated, branched or linear, lower-aliphatic diene,  
35 in particular having 4, 5 or 6 carbons, such as butadiene, 1,3-pentadiene, isoprene, 2,3-dimethylbutadiene, 1,3-hexadiene, and/or the fully or partly hydrogenated derivatives thereof. Particularly

advantageous properties have been achievable with isoprene.

The preparation of block copolymers of this kind is known per se. Where styrene is used as A block and isoprene as B block, the terms S-I and S-I-S block copolymers are used as well. One adhesive composition of the invention uses block copolymers of this kind having a diblock fraction of more than 40%, preferably of more than 55%, more preferably of more than 70%. Block copolymers of this kind are available commercially, examples being Kraton<sup>TM</sup> D 1119 (Kraton Polymers, 66% diblock fraction) and Quintac<sup>TM</sup> 3520 (Zeon Chemicals, 78% diblock fraction). The diblock fraction, here and below, is the fraction, as a proportion of the entirety of the block copolymers, of molecules containing one block A and one block B as defined above, these blocks being joined to one another, if desired, by constituent units which are not part of the blocks.

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By a sulfonated copolyester is meant, here and below, not only linear but also branched sulfonated copolyesters. Particular preference is given to using copolyesters which have a difunctional sulfo monomer unit with at least one -SO<sub>3</sub>H or -SO<sub>3</sub>M functionality (M = metallic counterion) on a preferably aromatic nucleus. Preferred aromatic nuclei are benzene, naphthalene, anthracenes, biphenyl, oxybiphenyl, sulfonylbiphenyl, and methylenebiphenyl. Particularly preferred difunctional sulfo monomer units are 5-sodium sulfonate isophthalic acid, 5-sodium sulfonate isophthalate, 5-lithium sulfonate isophthalic acid, and bis(2-hydroxyethyl)-5-sodium sulfonate isophthalate. Within the backbone of the sulfonated copolyesters, especially branched copolyesters, the stated sulfo monomer units are arranged preferably in random distribution; this can be achieved, for example, by copolymerization into the polymer backbone. The preparation of sulfonated

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copolyesters of this kind, especially branched copolyesters, is known per se. Those available commercially are, in particular, branched, sulfonated copolyesters containing the sulfo monomer unit 5-sodium sulfonate isophthalic acid, e.g., Eastman<sup>TM</sup> AQ 1950.

Surprisingly it has now been found that through the combination of elastomeric block copolymers with a high diblock fraction and sulfonated copolyesters, especially branched copolyesters, it is possible to obtain adhesive compositions which have an improved wet peel strength. The dry and wet peel strengths were determined by means of a method corresponding substantially to the technique disclosed in the document US 5,028,485, column 4, lines 20-38.

In one particularly preferred embodiment of the invention the adhesive composition contains 10% - 40% by weight of at least one copolymer having a diblock fraction of more than 40%, preferably of more than 55%, more preferably of more than 70%, 5% - 30% by weight of a sulfonated copolyester, in particular a branched copolyester, 20% - 60% by weight of a tackifier, 10% - 30% by weight of a plasticizer, and preferably at least one auxiliary, in particular a stabilizer.

By tackifiers are meant, here and below, resins in particular. In the context of the invention it is possible with preference to use natural and modified resins, examples being gum resins, wood resins, colophony resins, oil resins, distilled resins, hydrogenated resins, and dimerized and polymerized resins. Additionally use may also be made of esters, especially glycerol or pentaerythritol esters of natural or modified resins, particularly glycerol esters of wood resins, glycerol esters of hydrogenated resins or the like; furthermore, it is also possible to employ aliphatic, aromatic or mixed aliphatic/aromatic

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hydrocarbon resins and phenolically modified terpene resins or their hydrogenated derivatives. For particular applications it is of course also possible to use mixtures of the stated tackifiers. A tackifier  
5 for use with particular preference in the context of the invention is Foral<sup>TM</sup> 85-E from Eastman<sup>TM</sup>, an ester of a hydrogenated resin.

By plasticizers are meant, here and below, substances  
10 which can be added to the adhesive composition in order to enhance its processing and elastic properties, especially flexibility and stretchability; an additional action as a plasticizer is possible. Plasticizers commonly for use in the context of the  
15 invention are, in particular, polyesters, epoxides, phosphoric acid derivatives, phthalic acid derivatives, isophthalic acid derivatives, biphenyl derivatives, maleic acid derivatives, glycolates, citric acid derivatives, benzoic acid derivatives, adipic acid  
20 derivatives, castor oil, mineral oils, and glyceryl trihydroxyoleate, and also liquid, hydroxylated fatty acids and/or conjugated fatty acids, isostearic acid for example. A plasticizer for use with preference in the context of the invention is available commercially  
25 from BASF under the name VISTANEX<sup>TM</sup> PAR 950, a medium-molecular mass polybutene.

By auxiliaries are meant, here and below, substances including, in particular, inorganic diluents or fillers  
30 (examples being calcium carbonate, zinc oxide, titanium oxide, talc, carbon black, clays or the like), UV absorbers, heat stabilizers, release agents, anti-stick agents, and antioxidants. Preferred antioxidants for use in the adhesive compositions of the invention are  
35 available under the name IRGANOX<sup>TM</sup> from Ciba SC, especially Irganox 1010.

According to one particularly preferred embodiment of the invention the adhesive composition comprises as a copolymer component with a diblock fraction of more than 40%, preferably of more than 55%, more preferably  
5 of more than 70%, a styrene block copolymer, preferably a styrene-isoprene block copolymer. With block copolymers of this kind it has been possible to obtain particularly advantageous properties in respect in particular of the improved wet peel strength.

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In one further embodiment of the invention an adhesive bond which can be produced by the adhesive composition has a 180° wet peel strength of more than 8 N/m, preferably of more than 16 N/m, more preferably of  
15 24 N/m or more. The wet peel strengths were determined using a 23  $\mu$  polyester film backing material by means of a method corresponding essentially to the technique disclosed in the document US 5,028,485, column 4, lines 20-38.

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The adhesive composition of the invention is used with particular advantage to join natural or synthetic, especially textile, sheetlike structures to one another and/or to a second substrate, in particular the skin.  
25 The enhanced wet peel strength makes it possible in particular to ensure a durable bond in a moist environment.

The invention also relates, furthermore, to methods of  
30 joining substrates using an adhesive composition of the invention, and in particular of joining a substrate to the skin. The adhesive compositions of the invention can be employed with particular advantage in all methods of joining substrates where one of the key  
35 factors is an increased wet peel strength.

The invention relates, further, to products having at least one region which is prepared for joining to a

substrate, this region being provided at least partly with a coating comprising an adhesive composition of the invention. This may relate, inter alia and in particular, to a natural or synthetic, especially  
 5 textile, sheetlike structure and/or an adhesive tape. One preferred area of application in particular is that of medical adhesive tapes or adhesive sections on, for example, surgical drapes, but in particular also patches, ECG electrodes or the like. The adhesive  
 10 compositions of the invention fulfill outstandingly the wet peel strength and skin compatibility requirements that are high particularly in these areas of application.

15 The invention is elucidated in more detail below, with reference to exemplary embodiments, without the subject matter of the invention being restricted to these exemplary embodiments.

	% Diblock	A*	B*	C*	D	E
Kraton D 1111	15	4.6	4.1	-	-	-
Kraton D 1112	38	14.8	13.3	-	-	-
Europrene SOL T 190	25	5.7	5.1	-	-	-
20 Kraton D-1119P	66	-	-	-	22.6	-
Quintac 3520	78	-	-	25.1	-	22.6
AQ 1950		-	10.0	-	10.0	10.0
Foral 85-E		51.2	46.1	51.2	46.0	46.0
Vistanex PAR 950		22.7	20.4	22.7	20.4	20.4
Irganox 1010		1.0	1.0	1.0	1.0	1.0
Viscosity in mPa*s (160°C)		4200	1700	4000	2400	4300
180° peel strength (N/m), dry		140	260	308	272	276
180° peel strength (N/m), wet		2.0	6.4	16.0	8.8	24.0

Table 1: Adhesive compositions (A\*, B\*, C\*: comparative experiments; D, E: inventive adhesive compositions) and  
 25 their dry and wet peel strengths



Table 1 shows the composition of selected examples of inventive adhesive compositions (D and E) and also comparative experiments, which are marked by \* (A\*, B\* and C\*).

#### Ingredients of the adhesive compositions

Ingredients used in the adhesive compositions were the following, commercially available products: Kraton™ D-1111 (diblock fraction 15%), Kraton™ D-1112 (diblock fraction 38%), and Kraton™ D-1119P, all from Kraton Polymers; Europrene SOL T 190 (diblock fraction of 25%) from Polimeri Europa; Quintac™ 3520 (78% diblock fraction) from Zeon Chemicals; Foral™ 85-E from Eastman; Vistanex™ PAR 950 from BASF; and Irganox™ 1010 from Ciba SC.

#### Comparative experiments

Comparative experiment A\* shows an adhesive composition comprising a mixture of styrene-isoprene block copolymers with a low diblock fraction (15%, 38%, and 25%). Not only the dry peel strength but also the wet peel strength are inadequate for many areas of application. Even by adding a sulfonated copolyester in comparative experiment B\* it is already possible to achieve an improvement in dry and wet peel strength by a factor of around 2 or 3. The use of a styrene-isoprene block copolymer having a high diblock fraction of 78% in comparative experiment C\*, instead of the mixture of the block copolymers with a low diblock fraction, is able again to improve the wet peel strength in particular by a factor of approximately 2.5 as compared with comparative experiment B\*.

#### Inventive adhesive compositions

The adhesive compositions according to exemplary embodiments D and E combine the high diblock fraction of the block copolymer with the admixture of a sulfonated copolyester. Adhesive compositions D and E differ only in the differing diblock content of the block copolymer. From adhesive composition E in particular it becomes clear that with an inventive adhesive composition it is possible to achieve wet peel strengths which were not achievable with any of comparative experiments A\*, B\*, and C\*. A comparison in particular between comparative experiment C\* (no sulfonated polyester) and the adhesive composition E reveals a positive effect on the wet peel strength achievable.

Apart from this, the inventive adhesive compositions enjoy essentially the same advantageous processing and compatibility properties, in particular with respect to the skin, as are already known for adhesive compositions similar to comparative experiments A\*, B\*, and C\*.

#### Determination of dry and wet peel strengths

The dry and wet peel strengths were determined by means of a method corresponding essentially to the technique disclosed in the document US 5,028,485, column 4, lines 20-38.

This is a force measurement using a tensile testing machine. The parameter determined is the force required to detach an adhesive material, adhered under defined conditions to a certain test material, from that test material again, at a defined peel angle and at a defined speed. The tensile testing machine used was an Instron<sup>TM</sup> 5565, the backing material a nonwoven Omnidrape from Paul Hartmann. The sample under test is likewise applied to a surgical drape of this kind (test strip 25 mm wide and 150 mm long; coat weight 50 g/m<sup>2</sup>)

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and bonded to the backing material. Bonding is accomplished by over-rolling once with a 0.5 kg press roller. The adhered test strips are tested dry after 30 minutes; for determining the wet peel strength, the

5 bonded specimens are wetted after 30 minutes with 2 ml of deionized water, and tested after a further 5 minutes. The measurement is made with a peel angle of 180° and a peel speed of 300 mm/minute. The values reported correspond to the average from 4 independent

10 measurements.